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Electrical conductivity of polar dielectric monocrystal $NaNO_2$ under temperature influence in vacuum

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Sodium nitrite crystals were obtained from a melt by the Kyropoulos technique. The temperature dependence of the direct-current electrical conductivity $\sigma_{dc}(T)$ of $NaNO_2$ single crystal (sp. gr. *Im2m*) oriented along the polar direction [010] (crystallographic axis b) was studied by impedance spectroscopy under conditions of temperature exposure in a vacuum of $\sim 10^{-1}$ Pa. Impedance measurements were performed in three heating runs at 293−470 K. It was found that thermal exposure in a vacuum on a $NaNO_2$ crystal leads to a change in the ionic mechanism of electrical conductivity to a semiconductor one. During the first heating, the ionic conductivity of the crystal is equal to $7 \cdot 10^{-7}$ S/cm at 470 K. During the second and third heating, the conductometric data coincide with each other, the value of conductivity σ_{dc} increases by 70 times, reaching $5 \cdot 10^{-5}$ S/cm at 470 K. The temperature dependence $\sigma_{dc}(T)$ has a semiconductor character with an activation energy of electrotransfer of 81 ± 2 meV.

Keywords: sodium nitrite, functional materials, electrical conductivity, point defects.

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1. Introduction

Sodium nitrite $NaNO_2$ is a salt that is formed by a weak nitrous acid HNO_2 and a strong base NaOH. Crystals of a polar dielectric $NaNO_2$ have ferroelectric properties and belong to promising functional materials of electronics. Existence of ferroelectric properties in the $NaNO_2$ crystals was found in the 60s of the last century independently by Russian [1,2] and Japanese [3,4] scientists.

Sodium nitrite is a model crystal that is convenient for studying electrophysical properties of oxide ferroelectrics. Reliability of operation of the ferroelectrics in technical devices is limited by a value of their electrical conductivity. Electrical conductivity of the $NaNO_2$ crystals was investigated in the studies [5–11]. It was found that the nominally pure $NaNO_2$ crystals had pronounced dielectric properties and a low value of intrinsic electrical conductivity that has an ionic nature. The $NaNO_2$ crystals are highly hygroscopic and characterized by high sensitivity of the electrophysical properties to conditions of growth and external process effects.

It is known that crystals of oxide ferroelectrics (for example, $LiNbO_3$ [12–14]) can be transformed into a semiconductor state by reductive (including vacuum) annealing. According to data of the studies [12–14], an increase of a concentration of lithium vacancies V'_{Li} in the $LiNbO_3$ crystal (hereinafter defects are designated in Kröger-Wink symbols [15]) results in an increase of ionic conductance, while an increase of a concentration of oxygen vacancies $V_{\mathrm{O}}^{\bullet\bullet}$ that form donor centers results in an increase of *n*-type electron conductance.

The present study presents results of investigation of direct-current electrical conductivity $\sigma_{dc}(T)$ of the $NaNO_2$ single crystal in conditions of temperature impact at 293−470 K in vacuum and discusses a mechanism of electrotransport in sodium nitrite.

2. Structure and the electrophysical properties of the $NaNO_2$ crystals

A fusion temperature of the molecule-ionic crystals of the polar dielectric $NaNO_2$ is $T_{\mathrm{fus}} \approx 544$ [5,16], 553 K [17], which is significantly lower than the values of T_{fus} of ionic crystals of sodium gallides (for example, 1074 K for NaCl crystals). Further heating results in chemical decomposition of sodium nitrite at 593 K [16].

Shortly before fusion, $NaNO_2$ exhibited two closely spaced ferroelectric transitions: a Curie transition ($T_{\mathrm{C}} = 436.5$ [6,16], 437.2 K [17]) and a Néel transition ($T_{\mathrm{N}} = 437.5$ [16], 438 [5], 438.7 K [17]). These ferroelectric transitions are phase transitions of the „order–disorder“ type that are related to variation of orientation of complex anions NO_2^-, therefore, sometimes they say about orientational polymorphism in molecule-ionic sodium & nitrogen-containing oxides [16].

During the ferroelectric transitions, changes of symmetry of the $NaNO_2$ crystal are insignificant. At the room temperature, a structure of its ferroelectric phase belongs to a rhombic crystal system, space group *Im2m*; parameters of the rhombic lattice cell and a crystallographic density are $a = 3.569$ Å, $b = 5.569$ Å, $c = 5.384$ Å and

$\rho_X = 2.17\,\mathrm{g/cm^3}$, respectively [6,16]. Spontaneous polarization in the $NaNO_2$ crystals is directed along the axis b (of the crystallographic direction [010]) and related to orientation-ordered arrangement of the polar groups NO_2^- along this axis.

It is transformed from the ordered ferroelectric phase (space group *Im2m*) into the disordered paraelectric phase (space group *Immm*) via an intermediate incommensurate phase, whose temperature interval of existence is just $1-2$ K [16,17]. Between the Curie transition and the Néel transition, the incommensurate phase exhibits partial disordering of the polar groups NO_2^- along the crystallographic axis a. The high-temperature paraelectric phase exhibits a mirror plane m perpendicular to the axis b (space group *Im2m* → space group *Immm*), which results in equally-probable population of structure positions of the polar nitrite groups NO_2^-.

The molecule-ionic structure of the $NaNO_2$ crystals is formed by the polar groups NO_2^- and cations Na^+. The ferroelectric properties of these crystals are induced by dipole ordering of the complex anions NO_2^-, while their intrinsic electrical conductivity has the ionic nature and is induced by a low concentration of thermally-stimulate point defects.

According to data of the studies [6,8,9], ionic electrical conductivity of sodium nitrite is $2 \cdot 10^{-8}-6 \cdot 10^{-8}$ S/cm at 454 K. The $NaNO_2$ crystals were electrophysically measured [8] along the crystallographic axes a, b and c to detect slight anisotropy of electrical conductivity, which was 2–2.5 at 454 K. The temperature dependences of ionic electrical conductivity of the $NaNO_2$ crystals along the axes a, b and c exhibited conductance surges in 2–6 times at the ferroelectric transition $T_C = 433$ [8], 438 K [7].

Based on the ion-conductive $NaNO_2$ crystals, gas sensors for determining the NO_2 concentration were proposed [18,19].

3. Experimental

The performed conductometric experiments used a single-crystal sample $NaNO_2$, on which pyroelectric properties were measured in the study [20]. The single crystal was grown from a melt by a Kyropoulos technique and dyed in yellowish-brown tones. The same coloring of the $NaNO_2$ melt-grown crystals was mentioned in the study [9]. As noted in the study [20], such coloring is in inherent in the major part of all the polar oxide compounds. According to data of the studies [21,22], this fact indicates that a volume of the crystals includes color centers of the type $(V_O^{\bullet\bullet}, 2e')^\times$, which include oxygen vacancies and electrons.

Parameters of the rhombic lattice cell of the studied $NaNO_2$ crystal (space group *Im2m*) are $a = 3.57$ Å, $b = 5.578$ Å and $c = 5.39$ Å and well agree with the literature data [5,8]. The single-crystal sample was oriented along the crystallographic axis b of space group *Im2m* (it was prepared by cutting out along a cleavage plane). It was a plane-parallel plate of the thickness of 2.2 mm and the area of $15\,\mathrm{mm^2}$.

The study [20] included direct measurements of direct-current electrical resistance of this sample at the room temperature (Ag-electrodes, an electrometer 617 manufactured by Keithly). It turned out that its electrical conductivity was below 10^{-10} S/cm, which is related to the fact that this electrometer can not record resistances above $10^{10}\,\Omega \cdot \mathrm{cm}$.

Direct-current electrical conductivity σ_{dc} was determined indirectly from impedance spectra $Z^*(\omega) = Z' + iZ''$ (ω is a circular frequency) of the $NaNO_2$ single crystal with ion-blocking electrodes (Ag, C) within the range of frequencies $5-5 \cdot 10^5$ Hz and resistances $1-10^7\,\Omega$ (an instrument Tesla BM-507). An experimental installation and a procedure of the electrophysical measurements are described in the studies [23,24]. Impedance measurements allowed us to reliably determine bulk resistance R_b of the crystal from data of intersection of hodographs of impedance $Z^*(\omega)$ for the electrochemical cells with the axis of active resistances Z'. Values of specific ionic electrical conductivity were calculated by the formula

$$\sigma_{dc} = h/SR_b, \tag{1}$$

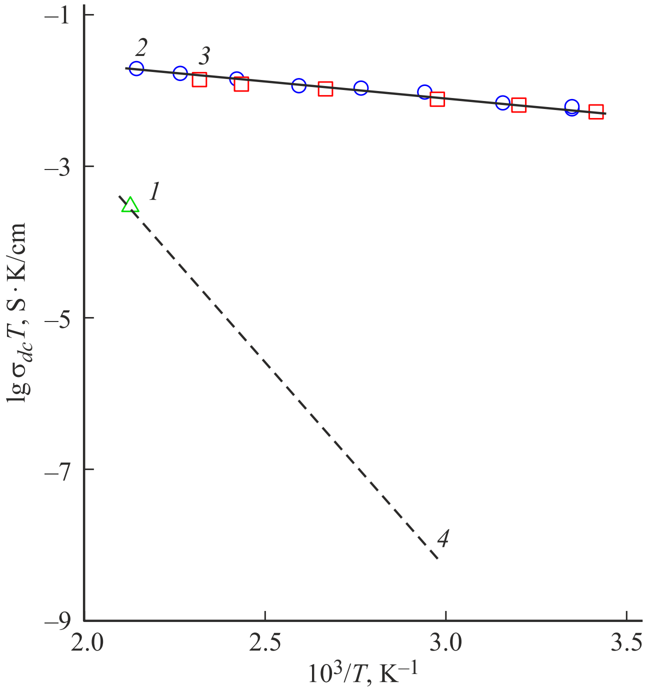
where h is a thickness of the crystal, S is an area of the electrodes. A relative error of electrical conductivity σ_{dc} is 5 %.

4. Discussion of results

The temperature measurements of impedance $Z^*(\omega)$ have been performed within the interval from the room temperature (293 K) to 470 K in the three heating modes. Pre-cleaned butt ends of the sample were coated with electrodes as a silver paste Leitsilber in the first and second heatings and a graphite paste DAG-580 in the third heating. The crystal was clarified after the first heating, which indicates partial disintegration of the color centers $(V_O^{\bullet\bullet}, 2e')^\times$.

Results of the measurements of electrical conductivity $\sigma_{\|b}(T)$ of the $NaNO_2$ crystal in the three temperature modes are shown in the Figure (the points *1–3*). During the first heating, ionic conductance was below a measurement limit of the instrument BM-507 ($\sigma_{dc} \ll 10^{-7}$ S/cm) almost for all the temperatures. Only ionic conductivity at 470 K could be reliably measured and it was $7 \cdot 10^{-7}$ S/cm. The obtained value of σ_{dc} well coincides with results of the studies for ionic conductance of $NaNO_2$ (see the Figure, the curve *4*) [5,7,8,11]. For comparison, ionic conductance of the $NaNO_2$ crystal is significantly lower than sodium-ion conductance of a superionic conductor of the NASICON type $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, which is $\sim 10^{-1}$ S/cm at 573 K [25].

Crystallochemically, basic intrinsic point defects in sodium nitrite are vacancies of sodium V'_{Na} and oxygen $V_O^{\bullet\bullet}$. Ionic radii of the cation Na^+ (1.02 Å [26]) and the anion



Temperature dependences of electrical conductivity of the $NaNO_2$ crystal along the crystallographic axis *b*: the experimental points *1, 2* and *3* are the first, second and third heating, respectively; the dashed line *4* is data from the study [5]. The solid line means joint data processing for the second and third heating according to the Arrhenius-Frenkel equation.

O^{2-} (1.38 Å) are highly different from a radius of the cation N^{3+} (0.16 Å).

It was crystallochemically analyzed to indicate that Na^+-ion transfer could be realized in the structure of the complex oxide $NaNO_2$. The following conditions contribute to higher mobility of the ions Na^+ in the structure of sodium nitrite. First of all, the cations Na^+ have a unit charge and a quite small value of the ionic radius for the singly-charged cations. Secondly, ionic bonds between Na^+ and NO_2^- are weaker as compared to covalent bonds N−O inside the polar groups NO_2^- [27].

Results of the study of ^{23}Na NMR (nuclear magnetic resonance on sodium nuclei) [28] directly indicate that it is the cations Na^+ that are responsible for ion transfer in the $NaNO_2$ crystals, wherein mobile defects are sodium vacancies V'_{Na} and a vacancy mechanism of electrical conductivity is realized. Formation of the vacancies V'_{Na} is a preferable method of creating a disordered subsystem of cations of alkali metals in crystal electrolytes [29], thereby resulting in the increase of mobility of the cations Na^+ in their structures. According to data of ^{23}Na NMR [28], diffusion motion of the ions Na^+ in $NaNO_2$ starts at the temperatures above ~ 450 K.

During the second and third heatings, a nature of behavior of electrical conductivity was sharply changed and conductometric data for these temperature modes are different from the data for the first heating. Between the second and the third heating, the silver electrodes were replaced with graphite ones and side surfaces of the sample were cleaned. It turned out that the conductometric data for the second and third heatings coincided between each other and they were jointly processed according to the Arrhenius-Frenkel equation:

$$\sigma_{dc}T = \sigma_0 \exp(-\Delta E_a/kT), \qquad (2)$$

where σ_0 is a pre-exponential factor of electrical conductivity and ΔE_a is energy of activation of electrotransport. The parameters of the Frenkel-Arrhenius equation are $\sigma_0 = 0.14\,\mathrm{S \cdot K/cm}$ and $\Delta E_a = 81 \pm 2\,\mathrm{meV}$.

It can be assumed that after heating in vacuum electrical conductivity of the $NaNO_2$ crystal has a semiconductor nature rather than an ionic one. The semiconductor nature of electrical conductivity is indicated by the following data. The value emerging electron conductance is $\sim 5 \cdot 10^{-5}$ S/cm at 470 K and exceeds ionic conductivity in ~ 70 times. The obtained value of electrotransport activation energy (81 meV) is highly different from the value of energy of activation of ionic conductivity in the $NaNO_2$ crystals: both in the ferroelectric range (0.90 eV [7]) and above the Curie point (0.72 eV [7]). The temperature dependence $\sigma_{dc}(T)$ does not exhibit any anomalies within the ferroelectric phase transitions ($T_{\mathrm{C}}, T_{\mathrm{N}}$). As noted above, in case of ionic electrical conductivity of the $NaNO_2$ crystals the conductance surges in 2−6 times were observed during the ferroelectric transitions [7,8].

Let us consider possible processes of formation of electron charge carriers during heating (annealing) the $NaNO_2$ crystal in vacuum. Since a band gap in the $NaNO_2$ crystal is $E_g \approx 3$ eV [30,31], then electron conductance has an extrinsic (impurity) nature. The most probable mechanisms of origination of electron conductance in the $NaNO_2$ crystal are the following processes. First of all, electrons can be delocalized from the color centers of the type $(V_{\mathrm{O}}^{\bullet\bullet}, 2e')^{\times}$ with their transition into a conduction band:

$$(V_{\mathrm{O}}^{\bullet\bullet}, 2e')^{\times} \rightarrow V_{\mathrm{O}}^{\bullet\bullet} + 2e'. \qquad (3)$$

Secondly, electrons can emerge due to escape of oxygen from the crystal lattice:

$$\mathrm{O}_{\mathrm{O}}^{\times} \rightarrow V_{\mathrm{O}}^{\bullet\bullet} + 2e' + 1/2\mathrm{O}_{2(\mathrm{gas})}. \qquad (4)$$

Detail investigation of the mechanism of electron conductance requires additional experiments.

5. Conclusion

We have analyzed the parameters of electrotransport in the $NaNO_2$ crystal under temperature impact in vacuum; the conductometric measurements have been performed in the three heating modes at 293−470 K. The initial crystal was dyed in the yellow-brown color, thereby indicating that it had the color centers of the type $(V_{\mathrm{O}}^{\bullet\bullet}, 2e')^{\times}$, which result in light absorption in the visible range. During the first heating, electrical conductivity of the crystal has the ionic nature: the value of conductance σ_{dc} is $7 \cdot 10^{-7}$ S/cm at 470 K. Ionic conductance is induced by migration of the sodium vacancies $V_{\mathrm{Na}}^{\bullet}$ formed when growing the NaNO$_2$ crystals, over the crystal lattice. Their contribution to total electrical conductivity of the dyed crystal is dominant as compared to the electrons.

It is found that temperature impact on the NaNO$_2$ crystal in vacuum results in replacement of the ionic mechanism of electrical conductivity with the semiconductor one, wherein the value of conductance of the crystal increases in ~ 70 times. Semiconductor conductance of the crystal is induced by jump motion of the electron carriers with the activation energy of $\Delta E_a = 81 \pm 2$ meV.

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Conflict of interest

The authors declare that they have no conflict of interest.

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